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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : G01N 27/12 | A2

(11) International Publication Number: WO 00/63682

(43) International Publication Date: 26 October 2000 (26.10.00)

(21) International Application Number: PCT/GB00/01343

(22) International Filing Date: 17 April 2000 (17.04.00)

(30) Priority Data:
9908696.9 17 April 1999 (17.04.99) GB

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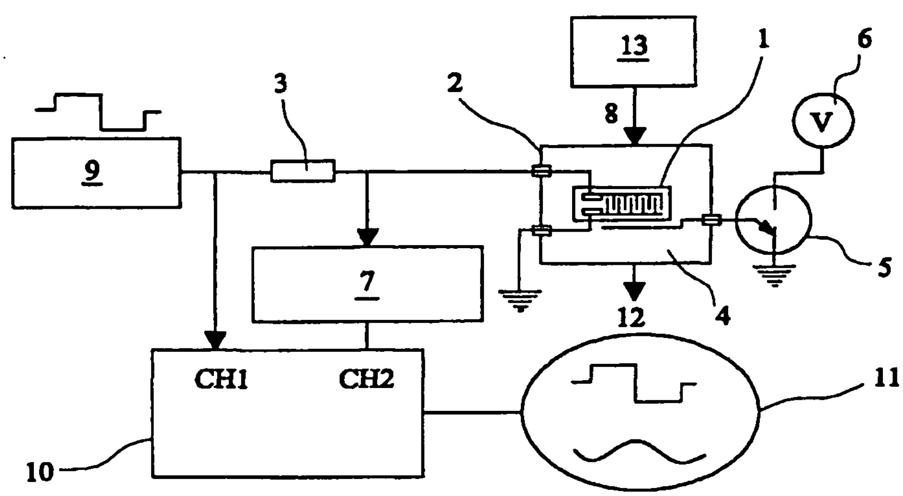
(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: SENSOR APPARATUS AND METHOD FOR DETECTING AND IDENTIFYING FLUIDS



(57) Abstract

An apparatus and method for improving the detection and identification of fluids by means of information obtained from one or more fluid sensors. These improvements are achieved by providing sensor means using very low conductive materials and forming different geometric patterns of electrodes on a sensor substrate. A low frequency bipolar excitation is used so as to provoke electrical reactions from the sensor means which are dependent upon the presence and/or concentration of one or more fluid components. A fluid delivery means allows the kinetics of the absorption and desorption process of the fluid sample to be included in the detection process. Further discriminatory information is also obtained in the relaxation of the sensor membrane following stimulus in either the time or frequency domain.

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SENSOR APPARATUS AND METHOD FOR DETECTING AND IDENTIFYING FLUIDS

The present invention relates to an apparatus and method for detecting and identifying fluids, and relates particularly to an apparatus and method for detecting fluid components by observing changes in electrical behaviour of one or more high impedance sensors in the presence of such fluids. By "fluids" it is meant samples of liquid and/or gas and/or vapour and combinations and/or mixtures of the same.

Many materials are known to undergo changes in electrical behaviour in the presence of fluids, primarily as a result of surface phenomena at the fluid/material interface, and which can be used to provide characteristic information to identify the fluid causing the electrical change.

This invention enhances changes in the electrical behaviour of high impedance sensor type materials and provides extra characteristic information in the presence of fluids. Although the exact mechanisms by which the changes in electrical behaviour of the sensor material are not fully understood, it is thought that the dynamic fluid flow across the sensor means combined with a constant bipolar excitation means causes two interrelated effects within highly resistive/non-conducting type sensor materials: -

Firstly, certain materials appear to have increased disorder effects within the structure at the molecular level promoting a skew in the normal distribution profile between insulator and conduction bands, particularly if they become de-polarised. This enables much higher

impedance materials to be used where 'Islands' of conductivity/charge differences appear to be formed within the sensor material and surface paths become more prominent. This results in the unexpected benefit of significantly increasing the material sensitivity and response time to fluids. It is probable that multiple conduction mechanisms are created through the material by hopping (phonon assisted quantum mechanical tunnelling) between one localised state (island) and another. The number of links/tunnels made appears to follow perculation theory. This invention enables new types of fluid sensors to be constructed using mixtures or combinations of low conductivity materials in order to create either real or virtual "islands" of conductivity within the sensor material. Alternatively the "islands" can be seen as "pockets" which fill or empty with sample fluid molecules as they dynamically absorb in or de-sorb out of the sensor material

Secondly, it also appears that some of the applied excitation energy is absorbed and promotes the number of free electrons/charge carriers within the sensor material to a higher state. The relaxation time of the excitation signal thus permits the material to emit spectral information as the material Lattice/structure realigns itself. This give the unexpected benefit of providing extra impedance information directly related to the surrounding fluid particularly in the frequency domain.

There are many conduction mechanisms through a sensor material and the present invention may enhance the fluid /material surface conduction paths that respond much

faster than the deeper mass bulk absorption conduction paths.

The constant low frequency alternating current (AC) bipolar excitation signal employed in the present invention causes a skew in the insulator/conduction band of highly resistive sensor materials. This invention exploits the dynamics of the impedance skew and depolarisation effects to detect fluid specie as the sample fluid absorbs or de-sorbs in or out of the sensor material.

Since about 1843 the Wheatstone bridge circuit configuration has been used to derive accurate measurements of sensor material resistance or impedance when using either a direct current (DC) or AC excitation signal respectively. This invention uses a high impedance fluid sensor and a resistor to form an AC half-bridge/potential divider circuit configuration. Measurement loading and distortion are minimised by buffering the output signal with a high impedance amplifier with good electrometer characteristics.

The reactance of the circuit is derived using either a simple or complex high voltage excitation signal and then converting the output using a standard transfer function H(s) based on Ohm's law. Further impedance characteristic information can also be derived using Fast Fourier transform (FFT) algorithms to convert the output impedance from the time to the frequency domain.

There are many electronic circuit configurations incorporating commercially available inter-digitated humidity sensing elements, which detect a static fluid as a

function of impedance. Resistive or capacitor type humidity detectors typically take many seconds or even minutes to equibralate to obtain a meaningful reading due to their thick film bulk effect operation.

Generally speaking, capacitor type humidity sensor circuits use AC excitation signals in the many kilohertz (Hz) range. Relatively low impedance and thick layers of sensor materials are used to reduce electrical noise levels. Capacitance type humidity sensors are normally operated over a small linear range directly proportional to the relatively slow, averaging and bulk absorption process.

Similarly, US Patent 5,571,401 discloses an array of "chemiresistors" for detecting analytes in fluids using conventional DC resistance measurement techniques which are subject to drift and offset problems. The relatively slow bulk resistance change of the sensor material is monitored as it swells in response to the fluid. The array of different "chemiresitors" produces an electrical pattern that distinguishes one fluid for use in an electronic nose system. The "chemiresistors" are formed on regularly spaced conducting elements using non-conductive organic polymer type materials combined with highly conductive non-organic material such as carbon black material. Changing the mixture modifies the chemical response and the bulk effect resistance.

GB 2203553 discloses a single gas sensor in which a layer of semi-conducting organic polymer such as polypyrrole is subjected to an alternating electrical signal. The frequency range used is varied or sweeps from 1 MHz to 500 MHz, and the variation in impedance characteristics of the

organic polymer layer is obtained as a function of frequency in the presence of a gas to be detected. The variation in electrical behaviour is function of frequency that is used to identify the presence of a particular gas.

Similarly, US patents 4,795,968 and 4,864,462 both disclose systems that use low impedance rare earth type materials as a dielectric. Gas species and concentrations are derived from a capacitor type sensor by sweeping the applied frequency (0.1 to 30Hz) and voltage amplitude (1 to 100milli volts). These complex alternating voltage and frequency systems are used primarily to chart the changes in the diode type bulk response of the rare earth material to the surrounding gas. Other changes in the low impedance characteristics are also determined from monitoring the harmonic distortion using phase detection hardware circuitry.

The arrangements disclosed in patents GB 2203553, US patents 4,795,968 and 4,864,462 above, suffer from a number of drawbacks, including that the frequency scanning and sweeping technique involved are time consuming, and the necessary hardware is expensive. In addition, it is believed that the result is brought about by the many complex and inter-related factors which may vary throughout the course of the relatively long duration of the scanning process, thus limiting the reproducibility of measurements, and which in turn may limit the accuracy with which gases may be detected.

UK Patent GB9608774.7 discloses a system which primarily uses a series of uni-polar excitation pulses to transform a gas sensor response from the time domain to the frequency

domain utilising linear integral transforms of the Fast Fourier type. Signal conditioning is performed on both the excitation signal and sensor response to modify the bandwidth and select a frequency range of interest. This is achieved using one or more uni-polar pulses substantially between 1ms to 1 μs (1KHz- 1MHz) in duration to pre-excite a sensor before the FFT measurement pulse. The excitation pulses used are strictly defined and restricted by the FFT and sampling theory that is very evident in this patent.

The time and duration differences of the excitation and FFT measurement pulses disclosed in UK Patent GB9608774.7 has the potential to introduce noise by disturbing the equilibrium/skew conduction conditions of the sensor material.

Preferred embodiments of the present invention seek to overcome or reduce the above disadvantages of the prior art.

According to a first aspect of the invention, there is provided an apparatus for detecting a fluid, the apparatus comprising: sensor means having electrical properties dependent upon the presence and/or concentration of a fluid, a fluid delivery means to expose the fluid to the sensor means, an excitation means for applying a bipolar ac excitation of fixed frequency, amplitude and shape to the sensor means, a detector means for detecting the behaviour of the sensor means in response to the excitation and fluid means, and transforming means for transforming an output of the detector means to determine an electrical transfer function of the sensor means in the presence of said fluid.

Preferably, the sensor means comprises one or more sensor

means, each of which comprises a combination of first and second electrodes with one or more layers of one or more materials having electrical properties dependent upon the presence and/or concentration of one or more fluids.

The or each layer may comprise one or more sensing materials having a resistivity substantially greater than or equal to 10^{+6} Ohm meters.

Preferably, the or each sensor means comprises a conductive pattern formed on a sensor substrate comprising one or more sensor materials.

The conductive pattern may comprise the first and second electrodes being arranged in a regular or irregular geometrical construction.

The conductive pattern may comprise first and second spaced apart electrodes, each having a plurality of interconnected finger elements, the elements of the first and second electrodes being inter-digitated.

The separation between adjacent electrode elements of the or each sensor means is preferably substantially greater than 100μm.

The conductive pattern of the or each sensor means may comprise a body portion of electrodes of a given effective length with conductive material of various geometrical configurations and/or patterns dispersed between the body portion of the electrodes in order to change the electrical properties of the sensor.

The conductive pattern may comprise first and second spaced apart electrodes and a plurality of spaced apart conductive strips arranged in the gap between the two electrodes.

The strips may comprise elongated lengths of conductive material of substantially the same effective length as the first and second electrodes.

The elongated lengths of conductive material may be arranged in parallel relation to one another and the body portion of the electrodes and regularly spaced apart from one another within the gap. Such an arrangement effectively forming a series of mini-capacitors.

Alternatively, the elongated lengths of conductive material may be arranged in parallel relation to one another and the body portion of the electrodes, with the strips being irregularly spaced apart.

The conductive pattern may comprise first and second spaced apart electrodes and a plurality of spaced apart conductive islands of dimensions substantially less than the effective length of the electrodes and arranged in the gap between the two electrodes.

The islands may be irregularly or regularly arranged within the gap.

The thickness of each said layer in the sensor means may be substantially greater than 1μm

The excitation means preferably provides a bipolar excitation waveform at a fixed frequency with a repetition rate substantially in the range of between 16 seconds and 1 millisecond, the amplitude of the excitation being preferably within the range of 1 volt to 1000 volt peak value.

Preferably, the detector means connected to the sensor means has an input impedance substantially greater than or equal to 1 Mega Ohm.

An ac or dc voltage excitation may be used on the underside of the sensor substrate to modify the electrical properties dependent upon the presence and/or concentration of one or more fluids of the sensor means

The transforming means may derive the transfer function in either the time or frequency domain of the sensor means.

The transformation may be a linear intergral transformation such as a Fourier transformation or Fast Fourier transformation (FFT)

Identification and or storage means for identifying one or more fluid components from the output of the transforming means is preferably provided.

Preferably, there are provided a plurality of sensor means comprising an array of sensors constructed on a single substrate, the sensors having differing electrical properties dependent upon the presence and/or concentration of one or more fluids.

Preferably, there are provided a plurality of sensor means housed in a modular of a fluid sampling chamber.

The modular fluid sampling chamber may comprise a plurality of sampling chambers which are interconnectable, each sampling chamber containing a different sensor means.

Preferably, a fluid delivery means exposes fluid to one or more sensor means to measure reproducible changes from baseline conditions.

The apparatus may further comprise a data base storing information relating to transfer functions of the sensor means in the presence of a variety of fluids and, wherein,

there is further provided processing means for finding a match between one or more of the stored transfer functions and one or more transfer functions output from the transforming means.

According to a second aspect of the invention, there is provided a method for detecting a fluid, the method comprising a fluid for exposure to sensor means, applying bipolar ac excitation of fixed frequency, amplitude and shape to the sensor means, said sensor means having electrical properties dependent upon the presence and/or concentration of the fluid, detecting by detector means the behaviour of the sensor means in response to the excitation and fluid means, transforming an output of the detector means to determine an electrical transfer function of the sensor means in the presence of said fluid.

The excitation may be provided at a fixed frequency repetition rate substantially in the range of between 16 seconds and 0.1 micro second.

The fixed frequency excitation means may be applied to the sensor means in a recurrent manner at a sufficient frequency to allow transformation of the detected response from the sensor means.

There may be provided a further step of comparing the transfer function of the sensor means in the presence of said fluid, with prestored transfer functions to find one or more closest matches.

The method preferably comprises the step of identifying one or more components of the fluid.

In a preferred embodiment of the present invention one or more fluid sensors are constructed using a plurality of

materials of varying properties. In preferred embodiments of the present invention, a fluid sample is passed over one or more sensor means and then removed. The performance of the sensor is dependent on the bi-polar excitation signal, physical dimensions, the chemical nature, morphology and the electrical nature of the sensor material used.

The performance of the apparatus and system as a whole is also dependent on the controlled delivery of a fluid sample to a combined fluid chamber volume containing the sensor means. The sensor materials used are either organic or non-organic in nature and may be deposited on to a non-conductive inter-digitated substrate. The regular or non-regular spaced electrode elements of the sensor can be constructed using a variety of manufacturing methods and materials including thick film deposition and photolithography.

In a preferred embodiment, the sensor means comprises one or more transducers, each of which comprises a pair of electrodes and one or more layers of material having electrical properties dependent upon the presence and/or concentration of one or more fluids. The electrodes of the or each fluid sensor may comprise a body portion having a plurality of projections interposed between corresponding projections of the other electrode.

By providing interposed (i.e. interdigitated) electrode projections, this has the advantage of providing a compact electrode pair construction at the same time as a large active surface area for both the electrode/sensor material and the sensor material/fluid interface. This construction enables the resulting electrical change to be recorded with significantly improved signal to noise ratio.

Said interposed electrodes may have regular or irregular separation of substantially greater than 100μm that permits standard thick film deposition techniques to be employed in the manufacturing process of the sensor. Larger separations in the electrodes also permit the sensor material to be less refined resulting in easier reproduction in manufacture. In a preferred embodiment, the thickness of each said layer can also be greater than 1 μm to ensure that the sensor material lies within or over the interposed electrodes.

The practical embodiments of this invention allow an increase in gap size and thickness of sensor materials that gives significant manufacturing advantages over the prior art.

In certain preferred embodiments of the invention, the base of the sensor substrate is excited with either an AC or DC potential in order to repel or attract fluid molecules in or out of the sensor material to change the fluid selectivity.

The or each sensor material layer may comprise one or more of the following in any combination: charge transfer complexes/electro-conductive salt composites, electro-conductive polymers and polymer composites, chemo-resistive semi-conductors, discotic liquid crystals, liquid crystals, polymeric conductors and semi-conductors, piezo-electric materials, lipids, biological molecules, host/guest materials, porphyrins and related compounds, organo metallic materials, metallo organics, Langmuir Blodgett films, amino acids or ceramics. The resistivity of these

and other sensor materials or mixtures not listed typically being in excess of 10^{+6} Ohm-meters

In more preferred embodiments, insulator type materials such as doped plastics and ceramics are used. These materials include for instance, Polyvinyl, Polyethylene, Polymaleic, Polystyrene, Polyisocyanate, Acrylic, Alkyd, melamine, urethane and polyester type compounds. These types of materials inherently offer stability over time, mechanical robustness, chemical resistance and ease of reproduction that give significant performance advantages over the prior art.

Alternative embodiments of the invention may incorporate discrete organic or inorganic particles of semi-conductive compounds in the non-conductive sensor membrane. The distribution of the particles within the membrane can be adjusted to modify the sensor response to a fluid.

The excitation means preferably provides constant electrical measurement signals to one or more sensor means. A preferred excitation signal is a bi-polar square wave voltage signal that can have almost any fixed duration within the range of 1ms to 16 seconds. In an alternative embodiment of the invention, a plurality of sensor means is excited either by a common excitation signal or by a plurality of excitation means.

This type of excitation provides the unexpected benefits and advantage previously discussed but it also reduces the effects of oxidation, tracking and electrical breakdown within the sensor means by preventing the migration of ions. Exciting the base or mounting of the sensor substrate

with either an AC or DC potential further enhances these benefits.

In a preferred embodiment, the excitation means is an alternating bi-polar 10V square wave at 125 Hz. A square wave signal is effectively made up of many frequency components and the buffered output from a high input impedance detector means is transformed using complex frequency domain (s) notation and techniques because of the multiple frequency components present.

An alternative embodiment of the invention employs simple sinusoidal excitations to derive a simple impedance function.

The detector means is arranged to detect the behaviour of the sensor means in response to the excitation means. By employing a detector means of a relatively high input impedance distortion and loading of the sensor means response is substantially avoided. In an alternative embodiment of the invention, a plurality of sensor means may be excited by a plurality of excitation means. In certain embodiments of the invention, the detector means may incorporate filters to enhance the electrical response from the sensor means. In such an embodiment, the detector means may contain a low and/or high pass filter means.

The transforming means preferably operates according to the transfer function H(s) of a sensor means circuit. The sensor circuit may form part of a half-bridge arrangement and the transfer function H(s) of a circuit is the ratio of the response Y(s) of the sensor circuit to the excitation means X(s).

In a preferred embodiment, the overall asynchronous system noise is minimised by the ratio metric transform function and differential nature of the circuit used. When a plurality of sensors are used with a common excitation signal the calculations on the sensor means can be carried out quickly. By carrying out this simple transform function many times, this provides the further advantage that an averaging method is used rendering the apparatus less sensitive to asynchronous system noise. This embodiment of the present invention may have considerable performance and noise reduction advantages over the prior art.

In preferred embodiments, the excitation signal X(s) and detector response data Y(s) from the sensor means is sampled at high speed and stored. As discussed previously, the relaxation of the excitation signal permits the sensor material to emit spectral information directly related to the surrounding fluid. The stored impedance data may be converted from the time to frequency domain using an FFT algorithm to reveal the spectral characteristics of the sensor and the surrounding fluid.

The apparatus preferably further comprises identification means for identifying one or more fluid components from the output of the transforming means.

According to another aspect of the invention, there is provided a method of detecting one or more fluids, the method comprising applying an excitation signal to a sensor means having electrical properties which vary dependent upon the presence and/or concentration of one or more fluids, detecting the response of the sensor means to

application of the excitation signal, and transforming the detected response from the excitation signal to provide the electrical characteristics of the sensor means as an impedance function in either the time or frequency domain.

The methods of the present invention preferably comprise applying a bi-polar excitation voltage to the sensor means, and subsequently applying a transforming function to the detector means.

In a preferred embodiment, the transforming step comprises of using a multi-channel digital oscilloscope to sample and store the excitation and output voltages of a half-bridge circuit configuration. Voltage samples are preferably taken at a predetermined point in time and the output function H(s) is derived. In an alternative embodiment the peak response maybe used instead of a predetermined point in time. The output function can be a voltage or an impedance function if a balance resistor in the half-bridge is known to the transforming means.

In an alternative embodiment of the invention the method preferably further comprises the step of subtracting an actual dynamic fluid response from a previous stored response in order to derive a differential result. This differential data reduction technique is useful when a background fluids or odours are a problem and a plurality of fluid sensors and or pattern recognition algorithm is used. This provides the further advantage that the subtraction method used renders the apparatus less sensitive to drift and reduces the data processing function of the transforming means possibly resulting in

considerable performance and noise reduction advantages over the prior art.

The method preferably further comprises the step of identifying one or more fluid components from the impedance transformation either in the time or frequency domain.

The methods may include any one or more of the features disclosed in relation to the apparatus of the first aspect in any logical combination and vice versa.

In embodiments of the invention the one or more sensor means may have geometrical or mechanical layout properties that change the electrical properties of the sensor material means so as to vary upon the presence and/or concentration of one or more fluids.

In a preferred embodiment of the invention, one or more fluid chamber means are interconnected and each may incorporate one or more sensor means to form a fluid sensor array.

Preferred embodiments of the present invention will now be described, by way of example only and not in any limitative sense, with reference to the accompanying drawings, in which: -

Figure 1 shows a system overview of a first embodiment of a gas sensor apparatus in accordance with the teachings of the present invention.

Figure 2 is a detailed view of a fluid sensor construction for use with the apparatus of Figure 1;

Figure 3 shows a schematic side view through the fluid sensor construction of Figure 2;

Figure 4 is a simplified equivalent electrical circuit to the fluid sensor construction of Figure 2;

Figure 5 depicts a side view of a simple model of electron conducting mechanisms in a high impedance material;

Figure 6 is a plan view of a simple two dimensional model of conducting mechanisms and islands of conductivity in a high impedance material;

Figure 7 shows an alternative fluid sensor construction to Figure 2 utilising parallel active elements at regular spacing intervals;

Figure 8 shows an alternative fluid sensor construction to Figure 2 utilising small regular spaced active elements;

Figure 9 shows an alternative fluid sensor construction to Figure 2 utilising parallel active elements at non-regular spacing intervals;

Figure 10 is an alternative fluid sensor construction to Figure 2 utilising a random sequence active elements between the electrodes;

Figure 11 shows a modified schematic side view through the fluid sensor construction of Figure 2;

Figure 12 is a schematic plan view of the flow chamber design of the apparatus of Figure 1;

Figure 13 is a cross section drawing through the flow chamber design of Figure 16;

Figure 14 is a diagram of a plurality of flow chambers connected in series to form a fluid sensor array;

Figure 15 is a time domain output from the apparatus of figure 1;

Figure 16 shows an impedance response H(s) plotted with water and then Butanol in water using the apparatus of Figure 1;

Figure 17 shows the subtraction and differential response of two sensor means to different fluids.

Figure 18 is a graph of a typical output response signal of the apparatus of Figure 1 a high voltage, very low frequency excitation; and

Figure 19 is a time to frequency conversion of the output response of Figure 18;

Referring in detail to Figure 1, the fluid delivery means (13) injects fluid through fluid inlet port (8) of a sample fluid chamber (2). In the embodiment shown in Figure 1, the fluid is dry gas or gas bubbled through a test liquid sample which maybe for identification, cleaning, or calibration purposes of the apparatus of Figure 1. The fluid passes from the input inlet (8) over the sensor means

(1) and out through the outlet port (12). The fluid sensor (1) in the fluid chamber (2) has one electrical connection to earth and the other to a series resistance (3). The mounting bracket/sensor guard (4) is switched by a switch (5) to either earth or connected to a bias voltage (6). A high impedance buffer circuit (7) connected to the sensor and resistor network, consists of a CA3140 field effect input operational amplifier circuit with good electrometer characteristics. The buffered output leads to a channel input on an oscilloscope (10). The signal generator (9) is preferably a Scopex type 14D-15 function generator providing up to a 10 Volt bipolar square wave excitation signal at 125 Hz to both the sensor/resistor network and the remaining channel on the oscilloscope (10). A PICO technology ADC-200 digital oscilloscope uses a personal computer (11) to store and display the data. A single sensor network is shown but a plurality of sensors can be used to create a sensor array system if more channels are available. The excitation signal generator in this example forms the excitation means. The gas sensor (1) and balance resistor (3) form the sensor means. The buffer circuit (7) and oscilloscope (10) form the detector means and the personal computer (11) forms the transforming , display and storage means as set out in the first aspect of the invention above.

In the embodiment shown in Figure 1, the transfer function H(s) of the sensor network given by the equation:

$$Equation\ 1: Transfer\ function\ H(s) = \frac{Detector\ \mathrm{Re}sponse\ Y(s)}{Excitation\ Signal\ X(s)}$$

Determining the transfer function is carried out by means of a simple transform utilising Ohms law with the excitation signal being directly measurable at the output of the signal generator (9) and the detector response being represented by the signal at the input of buffer (7). It will of course be appreciated that whilst Figure 1 shows the excitation signal and detector response being graphically displayed, practical embodiments will sample and store values of the detector response according to excitation signal by A/D converting and then storing in memory. This is a convenient and well-established method of obtaining impedance in either the time or complex frequency domain, and can typically be carried out whilst the excitation signal is being applied to the gas sensor. Furthermore, the use of such a simple transform enables many elements of a system to be added and analysed simultaneously, which in turn enables an assembly of one or more sensors to form an electronic analysis system. The resulting synergy of sensor transfer functions obtained from various reference fluids and sensors can be stored and recorded digitally in the digital processing computer (11) for comparison with other reference or unknown samples.

Referring to Figure 2, each of the fluid sensors means comprises a pair of electrodes (21) having 19 gold inter-digitated active elements (22) screen-printed on to a ceramic substrate (23) of approximately 11mm square. The 19 active elements have a track and gap separation of 0.2mm. This construction is coated with a film of thickness greater than 1µm, of material whose electrical behaviour (i.e. impedance) changes in the presence of one or more gases to be detected. The sensor material in the present embodiment is polyethylene glycol and acrylic. The

circular/gasket geometry in this particular design is a practical aim to limit fluid leaks when mounted in flow chambers such as shown in Figures 12 and 13.

Referring to Figure 3, a cross section/side view through the fluid sensor of Figure 2. The interposed active elements (22) are mounted on the ceramic substrate (23) with the sensing material (31) acting as a dielectric between the active elements. In an alternative embodiment to this example the sensing materials (31) may cover the active elements (22).

Figure 4 is an electrical equivalent circuit of the fluid sensor of Figure 2 and represents a greatly simplified model of a complex and dynamic component. It can be seen from Figure 2, that the electrical characteristics of the fluid sensor will have both resistive and reactive (i.e. capacitive and inductive) features, which will contribute to the impedance of the fluid sensor as a whole. The key elements of the circuit are the leakage resistance (Rp), Nominal Capacitance (C), Dielectric Resistance (Rda), Dielectric Capacitance (Cda). Series Inductance (L) and Series resistance (Rs). Small-unexpected reactive effects in the dielectric appear over time when it is exposed to a gas to be detected and this is probably caused by molecules absorbing and or desorbing at different rates.

Figure 5 depicts a side view of a simple model of multiple electron conducting mechanisms in a high impedance material. An excitation emf is present on the interposed active elements (22). The elements are mounted on a ceramic non-conducting substrate (23) with the sensor material placed in between. An emf in conducting materials normally

produces a bulk conduction effect represented by the large arrow (53). Other conducting mechanisms are also represented using different arrows. Random/drift electron flow (54), hoping (55) and tunnelling (58) are also shown. The surface phenomena (57) at the fluid/material interface (58) affects the absorption and desorption kinetics throughout the whole material resulting in a complex response being generated.

Figure 6 depicts a plan view of a simple two dimensional model of conduction probably created through the sensor material by hopping (phonon assisted quantum mechanical tunnelling) between one localised state (island) (61) and another. With a constant applied excitation the number of links/tunnels made appears to follow perculation theory which is also directly affected by the surrounding fluid possibly filing and emptying "pockets" within the material.

Figures 7,8,9 and 10 show alternative fluid sensor constructions and geometry to that of Figure 2. In a practical embodiment of the invention further conductive or active elements (22,72,82,92,102) are etched or screen-printed on to a sensor substrate (23) between body portions (21A) of the electrode (21). In certain embodiments of the invention, the active element material can be non-conductive organic or inorganic material suspended within the material.

The alternative arrangements of Figures 7,8,9, and 10 have parallel electrodes (21) having a body portion (21A) of an effective length L with the different conductive or active element geometry shown. The geometry of the elements can be used to manipulate or promote different conducting

mechanisms and improve and or change the overall sensor material response. The different constructions are also more resistant to problems associated with shorts across the active elements caused by contamination in the fluid. A brief description of each type of construction follows :

Figure 7 shows a parallel arrangement that forms a series of mini-capacitors to permit AC responses to pass while limiting the DC resistive bulk effects.

Figure 8 shows a regularly spaced "island" arrangement to promote hopping and tunnelling conduction effects within the sensor material as a fluid absorbs in or out.

Figure 9 is a parallel element arrangement that forms a series of mini capacitors but with different gap sizes. When the applied excitation signal is relaxed, a number of free electrons/charge carriers within the sensor material emit spectral information as the material Lattice/structure realigns itself. The different amounts of energy absorbed in the different gap sizes enhance the impedance information directly related to the surrounding fluid.

Figure 10 is a random arrangement of "islands" which promotes many of the conduction paths previously mentioned and may be used to reduce the overall bulk impedance. This geometry is particularly useful if a pulsed, noisy or random excitation is used to derive the sensor impedance characteristic.

Figure 11 is a view similar to that of Figure 3, showing a cross section/side view through a fluid sensor of a preferred embodiment of this invention. The mounting

bracket/sensor guard (111) is normally earthed. In an alternative embodiment of the invention, the guard is used as a capacitor plate to apply an AC or DC bias voltage on to the sensor material from underneath the substrate. The induced bias voltage can be used to attract or repel polar molecules (112) such as water and derive more fluid specie information.

Figures 12,13 and 14 show a modular fluid chamber design of the apparatus of Figure 1. This embodiment provides easy and simple construction with no cross-port drilling operations necessary. The design permits easy manufacture of a fluid chamber that is highly chemically resistive by using materials such as PTFE and stainless steel tube. The chambers are interconnected with the minimum of components while keeping the dead volume to a minimum.

Figure 12 shows plan view of the modular fluid chamber of approximately 25mm diameter. The fluid sensor (23) is mounted on to the body of the flow cell (121) and secured in to position by the mounting bracket (124). In an alternative embodiment of the invention the mounting bracket is biased with an emf to affect the response of the sensor material as previously described in Figure 11.

Figure 13 is a cross section view of figure 12 and shows the gas flow from the input port (135) to the output port (136) using two sensors. The two ports are constructed with stainless steel tube pushed directly in to the PTFE flow chamber block. The two securing screws (123) are tensioned to make a fluid tight seal between the sensor surface (137) and the circular knife edged rim (138) on the body of the flow chamber.

Figure 14 shows a plurality of fluid chambers of Figure 13 interconnected by stainless steel tube (139). The fluid enters at the input port (142) and travels through the

array to the exhaust port (143).

Figure 15 shows the 125 Hz, 10 V bipolar excitation (151) and the sensor response (152) plotted against time from the apparatus of figure 1. As will be understood by persons skilled in the art, in principle, any one of several transformation means could be used to derive the impedance function of the device. Any arbitrary time domain excitation can be used to measure a system transfer function. Thus, in general, potential and current steps and pulses, such as square wave, saw tooth wave, triangular wave, and various noise excitations can all be used.

Two stages of data manipulation are involved in obtaining the transfer function as a function of frequency from the response of the system to an arbitrary time domain perturbation, namely the excitation and response functions must be sampled and recorded in a time interval of interest, and then the transform of each must be computed and the simple or complex ratio calculated. In this embodiment the voltage response Y(s) to the excitation X(s)voltage was taken at midpoint (153) on the positive cycle as shown to derive the value of H(s).

Figure 16 shows a sensor means response H(s) to water and 4 % v/v concentrations of Butanol in water using the apparatus of Figure 1. Initially dry air is used to establish a baseline followed by 5 second controlled injection of the fluid sample. The absorb and de-sorb information of each cycle is shown. The resulting transfer function obtained from various reference fluids and sensors can be stored and recorded digitally in the computer digital processing unit (11) for comparison and correlation analysis of fluids.

Figure 17 is a graph of two sensor means that responds differently to 4% V/V concentrations of Butanol and

Butanone in water using the apparatus of Figure 1 and transform H(s). Each response shown is subtracted from the water to obtain a difference result. This data reduction technique is useful in subtracting background odours or finding differences in complex mixtures of fluids.

Figure 18 is a graph of the output response (181) to a 200 Volt bipolar excitation operating at 0.2 Hz of the apparatus of Figure 1. The initial 1 ms was removed to bring the response within the measurement range of the buffer amplifier and data capture equipment. The low frequency excitation permits the sensor material lattice/structure to relax and emit spectral impedance information directly related to the surrounding fluid. The sensor was constructed with liquid crystal sensor materials. The sample fluid was water and 4% V/V concentration of Butanol in water.

Persons skilled in the art will also appreciate, that electrical square waves have the general property that although an oscillator may drive them at one particular frequency, they produce excitations across a range of frequencies. The extra small surface effects in the impedance output appear as noise on the output response.

Figure 20 is a time to frequency FFT conversion of the frequency domain output and system responses similar to Figure 19. Convolution and cross correlation with the excitation signal permits the extremely small surface components of a binary fluid mixture to be extracted from the rest of the system noise. Two peaks are shown indication the presence of water (191) and Butanol (192). The operation of the apparatus shown in Figures 1 will now be described.

Initially a baseline value of the sensor means is taken by passing dry air through the one or more fluid chambers (2).

Air is blown through a sample liquid to pick up volatiles which are then carried by the carrier gas and injected via gas inlet (5) to the sample chamber (2). A fixed absorb and de-sorb cycle is used to create a dynamic flow the sample fluid across the surface of each of the sensor (1). The signal generator (9) applies a constant bipolar excitation signal of 10 Volts at 125 Hertz (3) to the sensors (1) and series balance resistor (3). The electrical response of the sensor (1) is buffered by a high impedance op-amp circuit (7). The two-channel digital oscilloscope (10) collects data and converts it to a digital form for the personal computer (11) to store and process. The computational function of the digital processing unit (11) then performs the transforming function to derive the impedance value of each sensor using a fixed sampling point in time.

In the example of Figures 16 and 17 the impedance Zc for each sensor was derived as follows :-

Equation 2 :
$$Zc = Rb \times \frac{(Va - Vx)}{(Vx - Vb)}$$

Where : Rb = Balance resistance (Ohms)
Va = Applied Excitation Voltage +Ve
Vb = Applied Excitation Voltage -Ve
Vx = Sensor response Voltage.

Figure 16 shows the impedance response from a single sensor reacting to water and water/butanol using the apparatus of Figure 1. After flushing with air to establish a baseline, the output waveform changes over time as the two fluid samples are injected in to the fluid chamber (2) and flushed out in sequence. The kinetics of the absorption and de-sorption process provide the extra discriminatory information about the fluid species.

Similarly from the graph of Figure 17 using the apparatus of figure1, it can be seen that two different sensor means respond differently to the fluids of Butanol and Butanone as they are each introduced and then flushed out of the flow chamber in turn.

In another embodiment of the present invention the apparatus of Figure 1 can be easily modified to obtain further discriminatory information in the frequency domain. For example if the excitation voltage is increased to over 100V and applied frequency lowered to 0.2 Hz the sensor material becomes stressed and relaxed accordingly. During the relaxation phase extra discrimination components can be extracted using a fast fourier transform to convert from the time to frequency domain.

By means of a suitable correlation technique known to persons skilled in the art, such as fuzzy logic or an artificial intelligence algorithm, a predetermined degree of correlation between the time or frequency domain impedance output of digital processor (11) and one or more reference values may be obtained to identify the presence and/or concentration of one or more gases. The correlation technique can be further improved by connecting multiple sensors together to form an electronic nose system.

As a result of the improved speed of sampling, reduced sensitivity to noise and ease of manufacturing sensors compared with the prior art, the apparatus 1 of Figures 1 can be used as part of a continuous monitoring process as part of a feedback control loop, for example in food and/or chemical production lines.

In contrast to the art, in embodiments of the present invention a high voltage, lower frequency bipolar AC excitation is constantly applied in conjunction with a low conductivity sensor material to derive the impedance

characteristic. In the more conductive sensor materials and mixtures of the prior art, the larger and slower bulk resistance effects have been found to mask or swamp the smaller conduction and faster surface effects that are more predominant in this invention.

In embodiments of the present invention, the use of low or semi-conductive sensor materials enables more of the smaller conduction mechanisms with faster response times to be measured. The improved fluid sensor response time enables better absorption and de-sorption kinetics of a sample fluid to be obtained for a given thickness or cross sectional area of sensor material that greatly enhances the quality of the information over the prior art. By dynamically injecting a sample fluid over a fluid sensor, the absorption and de-sorption response permits a chemically neutral sensor to act as a broad band molecular filter that can be used to detect fluid species. This gives the unexpected benefit of reducing possible poisoning effects of the sample fluid on the sensor and being able to sample fluids at a faster rate than the prior art. Non-neutral materials can also be used to make the apparatus of the invention respond to a narrower band of fluid specie.

In the present invention the skew in the insulator/conduction bands caused by the AC excitation also provides the unexpected benefit of being able to use sensor materials which were otherwise considered unsuitable, such as certain semi-conducting, plastic or ceramic type sensor materials which would ordinarily be considered non-conductive and/or chemically neutral using conventional DC measurement methods. This invention permits these types of materials to be employed to construct sensors that are inherently more robust, stable and easier to manufacture than the sensor devices used in the prior art. The low conducting sensor materials of this invention can also be combined and or mixed together to form other low power, low

cost high impedance sensor devices that respond differently to fluid species.

In particular embodiments of the invention, the high impedance response of a sensor material can be further modified using high voltage excitation with either regular or irregular spaced electrode elements. With non-regular construction of the electrode elements, the whole sensor construction can be "tuned" in to a useful range by altering the voltage or frequency of the excitation signal.

Unlike the prior art discussed previously, the bi-polar excitation signals used in embodiments of this invention are not limited by the constraints of FFT theory as the excitation is applied constantly. Maintaining a constant excitation signal maintains the sensor material equilibrium particularly if the material and or surrounding fluid such as water vapour can be polarised.

In selected embodiments of the invention, the harmonics of a high voltage relaxation cycle of a low frequency square wave excitation are detected using a Fast Fourier transform (FFT) algorithm to determine the sensor response characteristic. This overcomes many of the drift and noise problems associated with the slow frequency sweep excitation of the prior art.

It will be appreciated by persons skilled in the art that the above embodiment has been described by way of example only, and not in any limitative sense, and that various alterations and modifications of the invention are possible without departure from the scope of the invention as defined by the appended claims. For example, the apparatus may detect liquids and liquid/gas mixtures as well as gases, and the excitation may occur by means of excitations other than electrical excitations, for example optical, mechanical, infrared, acoustic, thermal or magnetic

excitation.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extend to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

Claims

1. An apparatus for detecting a fluid, the apparatus comprising:-

sensor means having electrical properties dependent upon the presence and/or concentration of a fluid, a fluid delivery means to expose the fluid to the sensor means, an excitation means for applying bipolar excitation of fixed frequency, amplitude and shape to the sensor means, a detector means for detecting the behaviour of the sensor means in response to the excitation and fluid means, and transforming means for transforming an output of the detector means to determine an electrical transfer function of the sensor means in the presence of said fluid.

2. An apparatus according to claim 1, wherein the sensor means comprises one or more sensor means, each of which comprises a combination of first and second electrodes with one or more layers of one or more materials having electrical properties dependent upon the presence and/or concentration of one or more fluids.

3. An apparatus according to claim 1 or 2, wherein the or each layer comprises one or more sensing materials having a resistivity substantially greater than or equal to 10^{+6} Ohm meters.

4. An apparatus according to claim 1, 2 or 3, wherein the or each sensor means comprises a conductive pattern formed on a sensor substrate comprising one or more sensor materials.

5. An apparatus according to claim 4, wherein the conductive pattern comprises the first and second electrodes being arranged in a regular or irregular geometrical construction.

6. An apparatus according to claim 4 or 5, wherein the conductive pattern comprises first and second spaced apart electrodes, each having a plurality of interconnected finger elements, the elements of the first and second electrodes being inter-digitated.

7. Apparatus according to claim 5 or 6, wherein the separation between adjacent elements of the first and second electrodes of the or each sensor means is substantially greater than 100μm.

8. An apparatus according to claim 4 or 5 wherein the conductive pattern of the or each sensor means comprises a body portion of electrodes of a given effective length with conductive material of various geometrical configurations and/or patterns dispersed between the body portion of the electrodes.

9. An apparatus according to claim 8, wherein the conductive pattern comprises the first and second spaced apart electrodes and a plurality of spaced apart conductive strips arranged in the gap between the two electrodes.

10. An apparatus according to claim 9, wherein the strips comprise elongated lengths of conductive material of substantially the same effective length as the first and second electrodes.

11. Apparatus according to claim 10, wherein the elongated lengths of conductive material are arranged in parallel relation to one another and the body portion of the electrodes and regularly spaced apart from one another within the gap.

12. Apparatus according to claim 10, wherein the elongated lengths of conductive material are arranged in

parallel relation to one another and the body portion of the electrodes, with the strips being irregularly spaced apart.

13. Apparatus according to claim 8, wherein the conductive pattern comprises the first and second spaced apart electrodes and a plurality of spaced apart conductive islands of dimensions substantially less than the effective length of the electrodes and arranged in the gap between the two electrodes.

14. Apparatus according to claim 13, wherein the islands are irregularly arranged within the gap.

15. Apparatus according to claim 13, wherein the islands are regularly arranged within the gap.

16. An apparatus according to any of claims 2 to 15, wherein the thickness of each said layer in the sensor means is substantially greater than 1μm

17. An apparatus according to any of the preceding claims, wherein the excitation means provides a bipolar excitation waveform at a fixed frequency with a repetition rate substantially in the range of between 16 seconds and 1 millisecond.

18. An apparatus according to any preceding claim, wherein the excitation has an amplitude between 1 and 1000V peak value.

19. An apparatus according to any of the preceding claims, wherein the detector means connected to the sensor means has an input impedance substantially greater than or equal to 1 Mega Ohm.

20. An apparatus according to any of the preceding

claims, wherein an ac or dc voltage excitation is used on the underside of the sensor substrate to modify the electrical properties dependent upon the presence and/or concentration of one or more fluids of the sensor means

21. An apparatus according to any of the preceding claims, wherein the transforming means derives the transfer function in either the time or frequency domain of the sensor means.

22. An apparatus according to claim 21 wherein the transformation is a linear integral transformation such as a Fourier transformation or Fast Fourier transformation (FFT)

23. An apparatus according to any of the preceding claims, further comprising identification and or storage means for identifying one or more fluid components from the output of the transforming means.

24. An apparatus according to any of the preceeding claims, wherein there are provided a plurality of sensor means comprising an array of sensors constructed on a single substrate, the sensors having differing electrical properties dependent upon the presence and/or concentration of one or more fluids.

25. An apparatus according to any of the preceeding claims, wherein there are provided a plurality of sensor means housed in a modular fluid sampling chamber.

26. An apparatus according to claim 25, wherein the modular fluid sampling chamber comprises a plurality of sampling chambers which are interconnectable, each sampling chamber containing a different sensor means.

27. An apparatus according to any of the preceeding

claims, wherein a fluid delivery means exposes fluid to one or more sensor means to measure reproducible changes from baseline conditions.

28. An apparatus according to any of the preceding claims, wherein the apparatus further comprises a data base storing information relating to transfer functions of the sensor means in the presence of a variety of fluids and, wherein, there is further provided processing means for finding a match between one or more of the stored transfer functions and one or more transfer functions output from the transforming means.

29. A method for detecting a fluid, the method comprising a fluid for exposure to sensor means, applying bipolar ac excitation of fixed frequency amplitude and shape to the sensor means, said sensor means having electrical properties dependent upon the presence and/or concentration of the fluid, detecting by detector means the behaviour of the sensor means in response to the excitation and fluid means, transforming an output of the detector means to determine an electrical transfer function of the sensor means in the presence of said fluid.

30. A method according to claim 29, wherein the excitation is provided at a fixed frequency repetition rate substantially in the range of between 16 seconds and 0.1 micro second.

31. A method according to claim 29 or 30, wherein the fixed frequency excitation means is applied to the sensor means in a recurrent manner at a sufficient frequency to allow transformation of the detected response from the sensor means.

32. A method according to claim 29, 30 or 31, wherein there is provided a further step of comparing the transfer

function of the sensor means in the presence of said fluid, with prestored transfer functions to find one or more closest matches.

33. A method according to any one of claims 29 to 32, further comprising the step of identifying one or more components of the fluid.

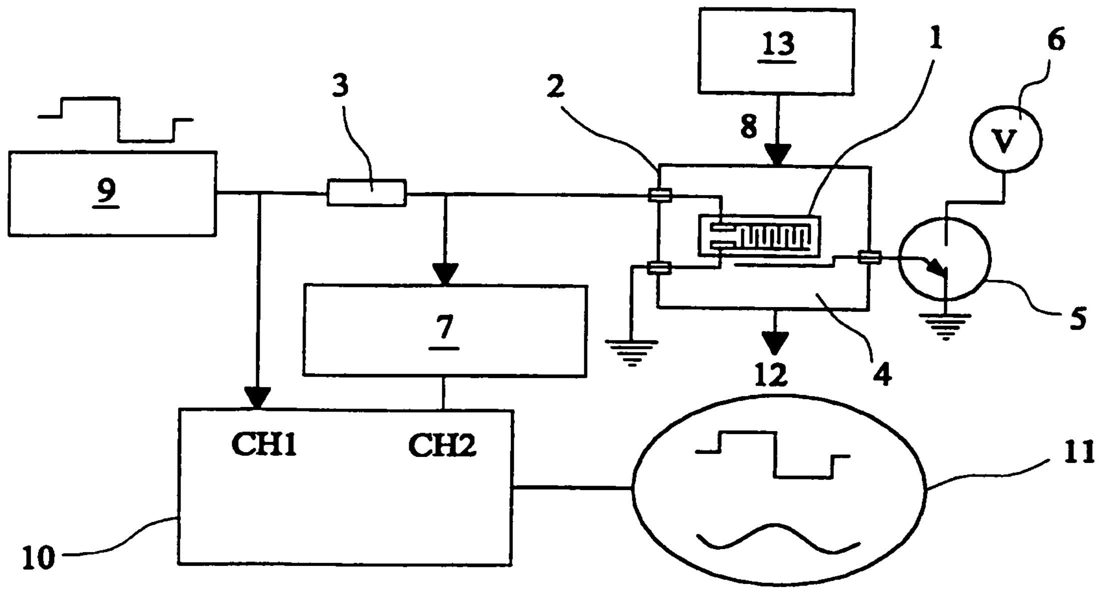


FIG. 1

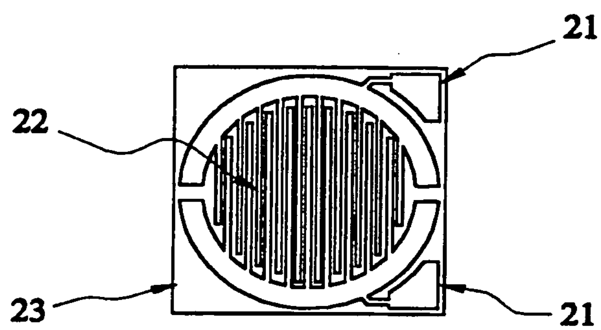


FIG. 2

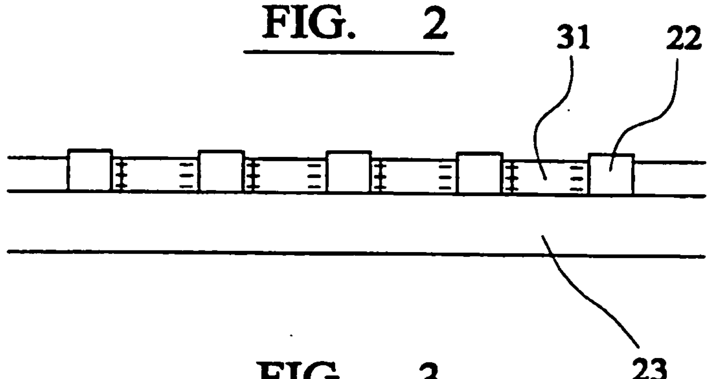


FIG. 3

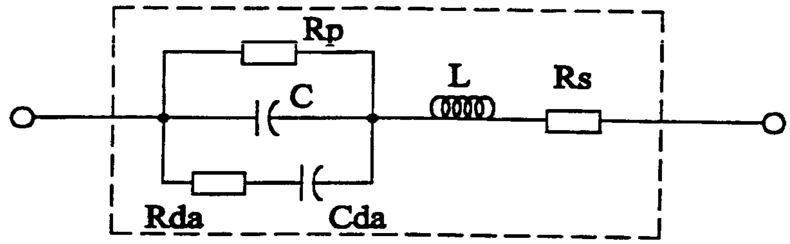


FIG. 4

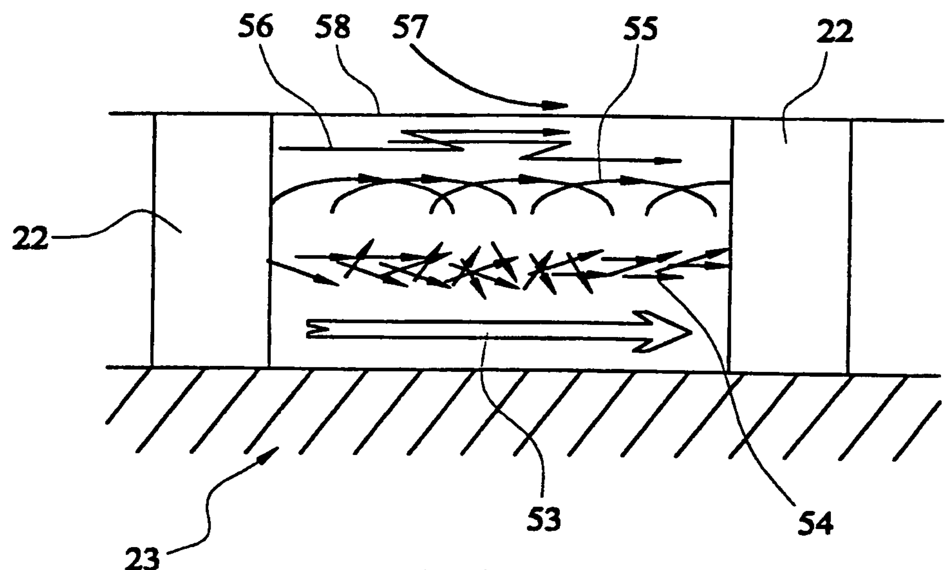


FIG. 5

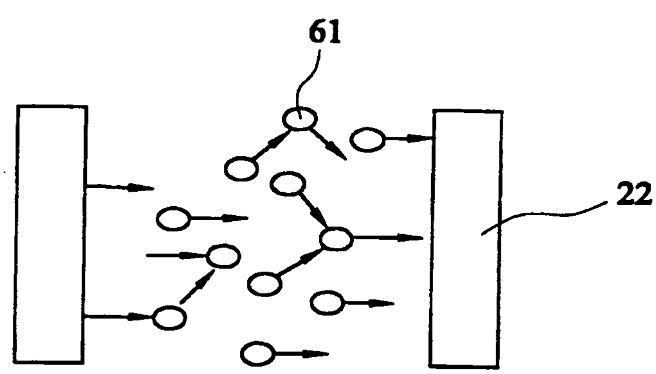


FIG. 6

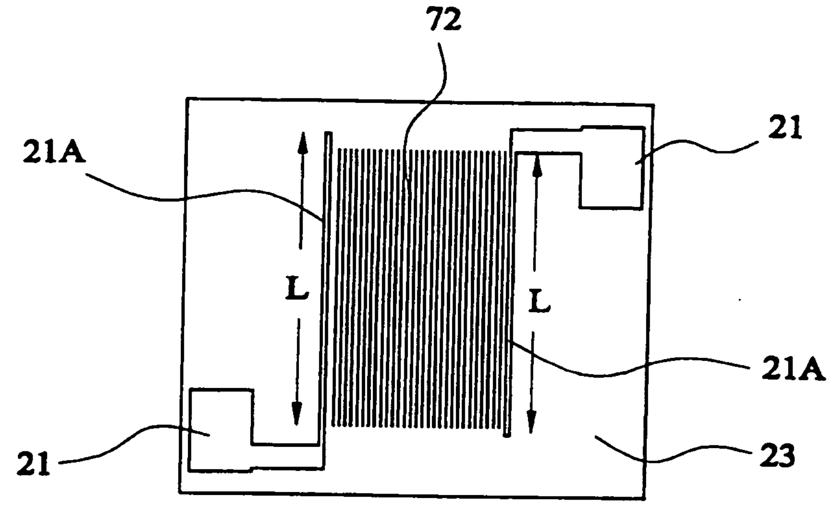


FIG. 7

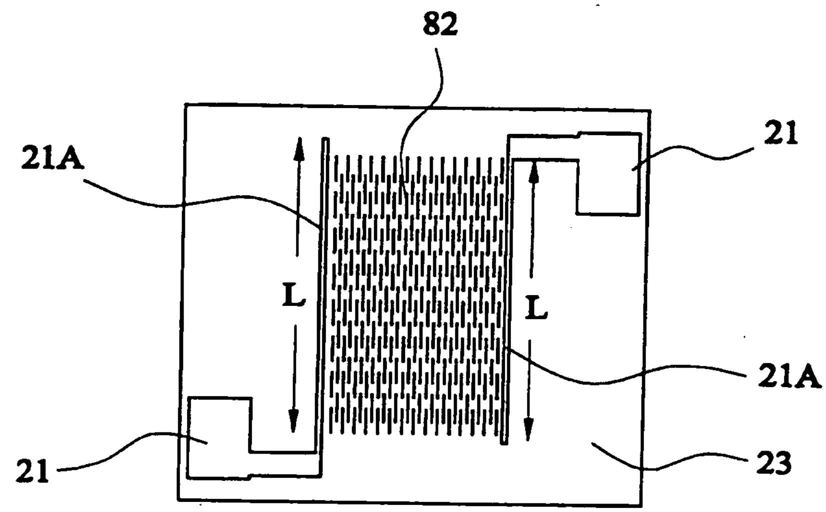


FIG. 8

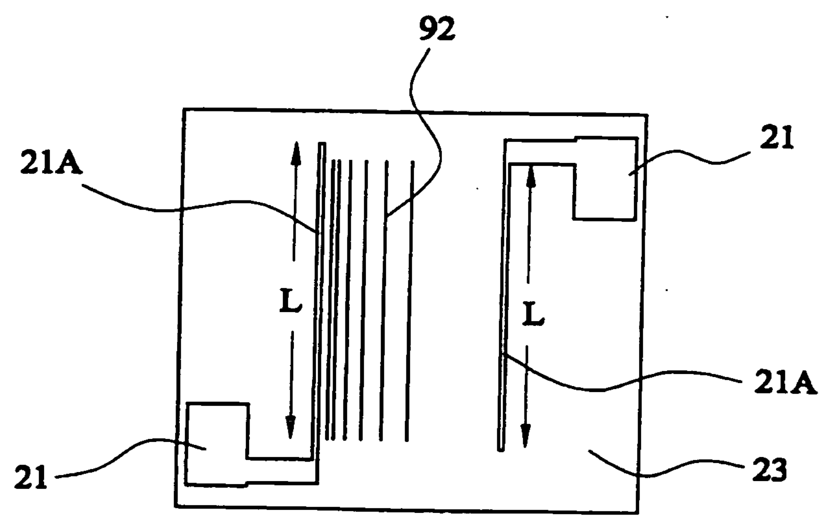


FIG. 9

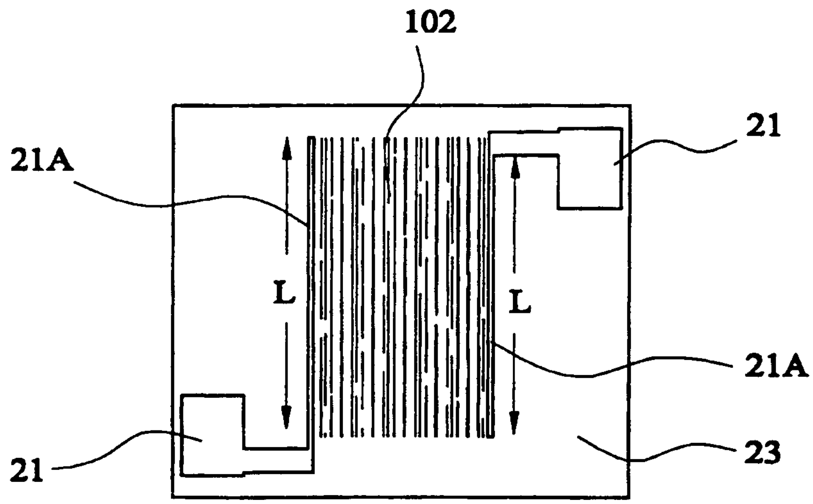


FIG. 10

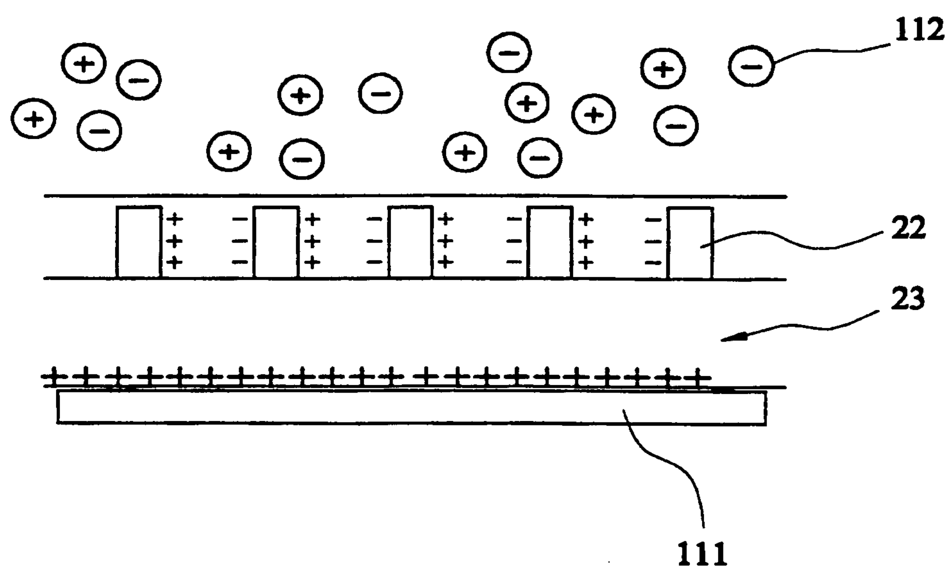


FIG. 11

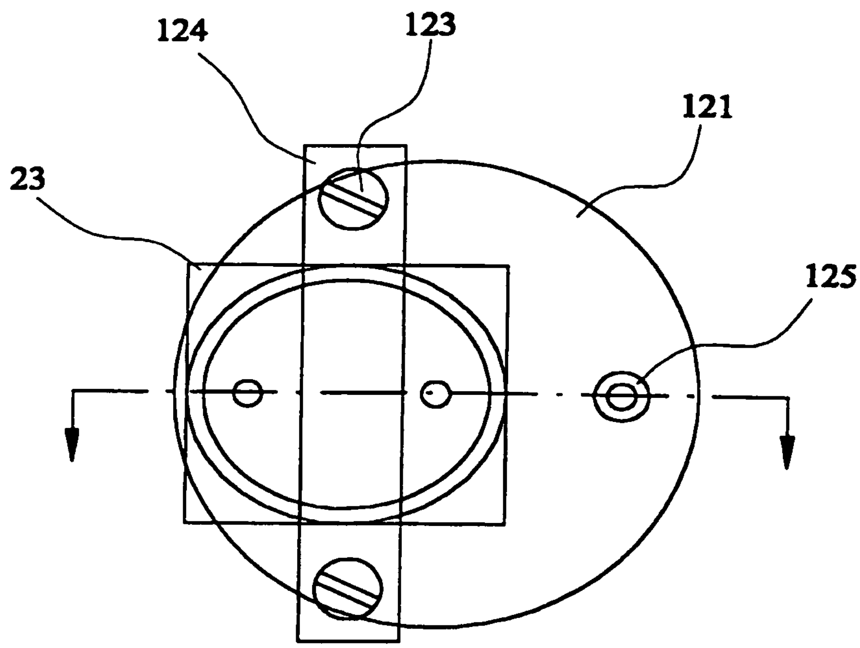
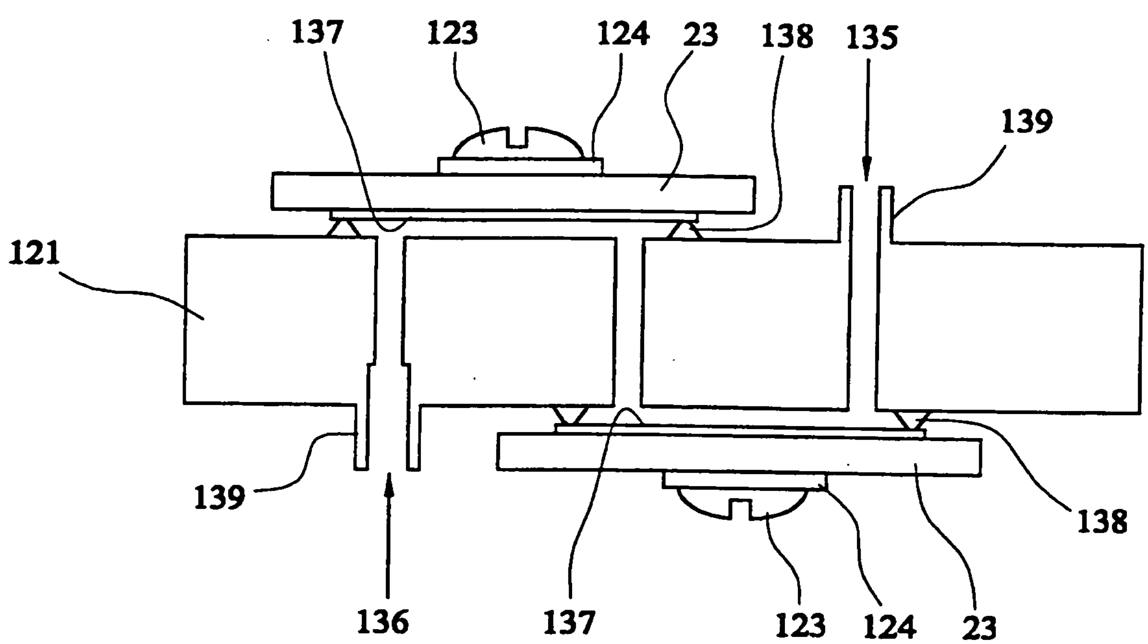

124
123
121
23
125

FIG. 12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23
138
135
139
121
139
136
137
123
124
23
138

FIG. 13

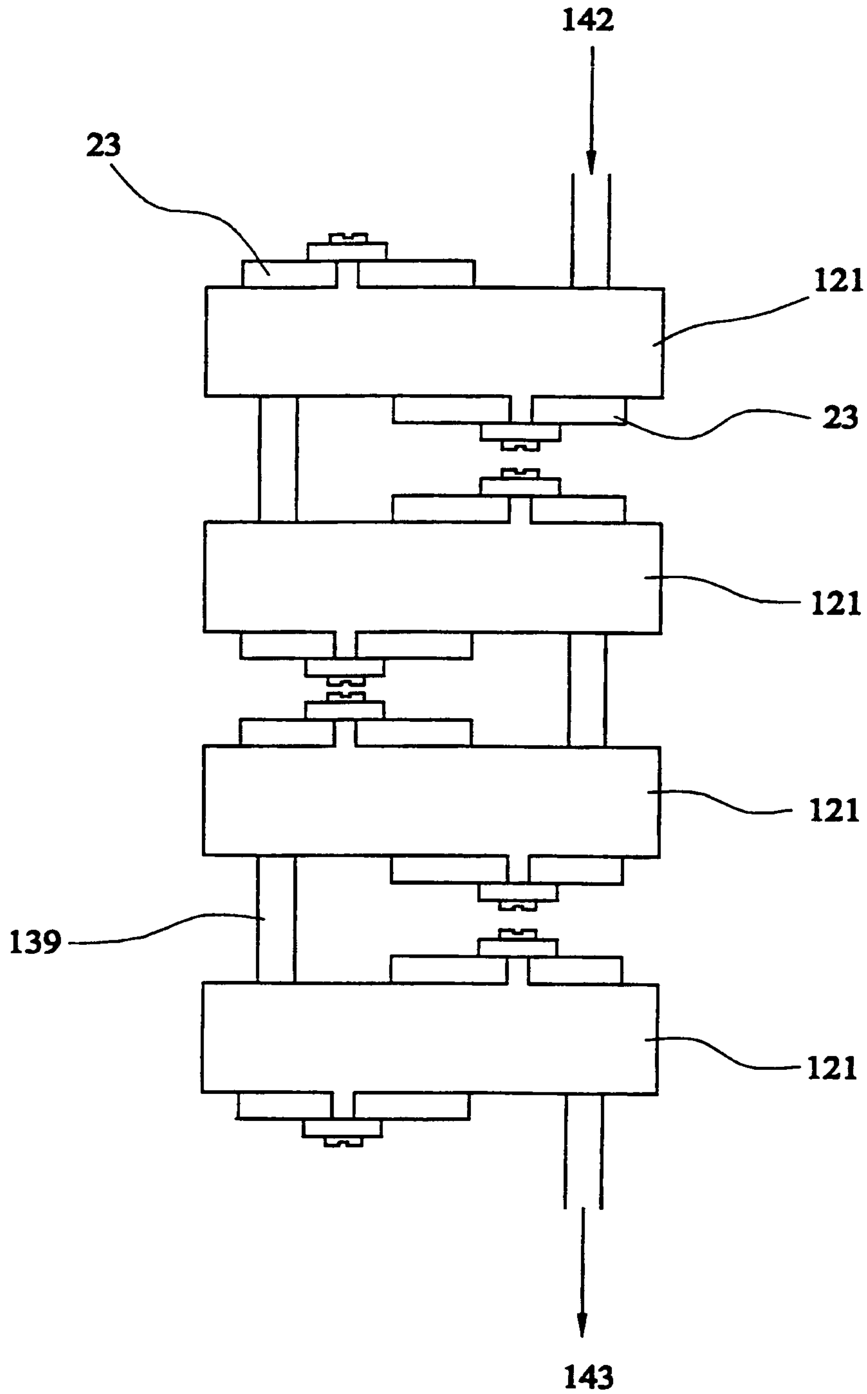
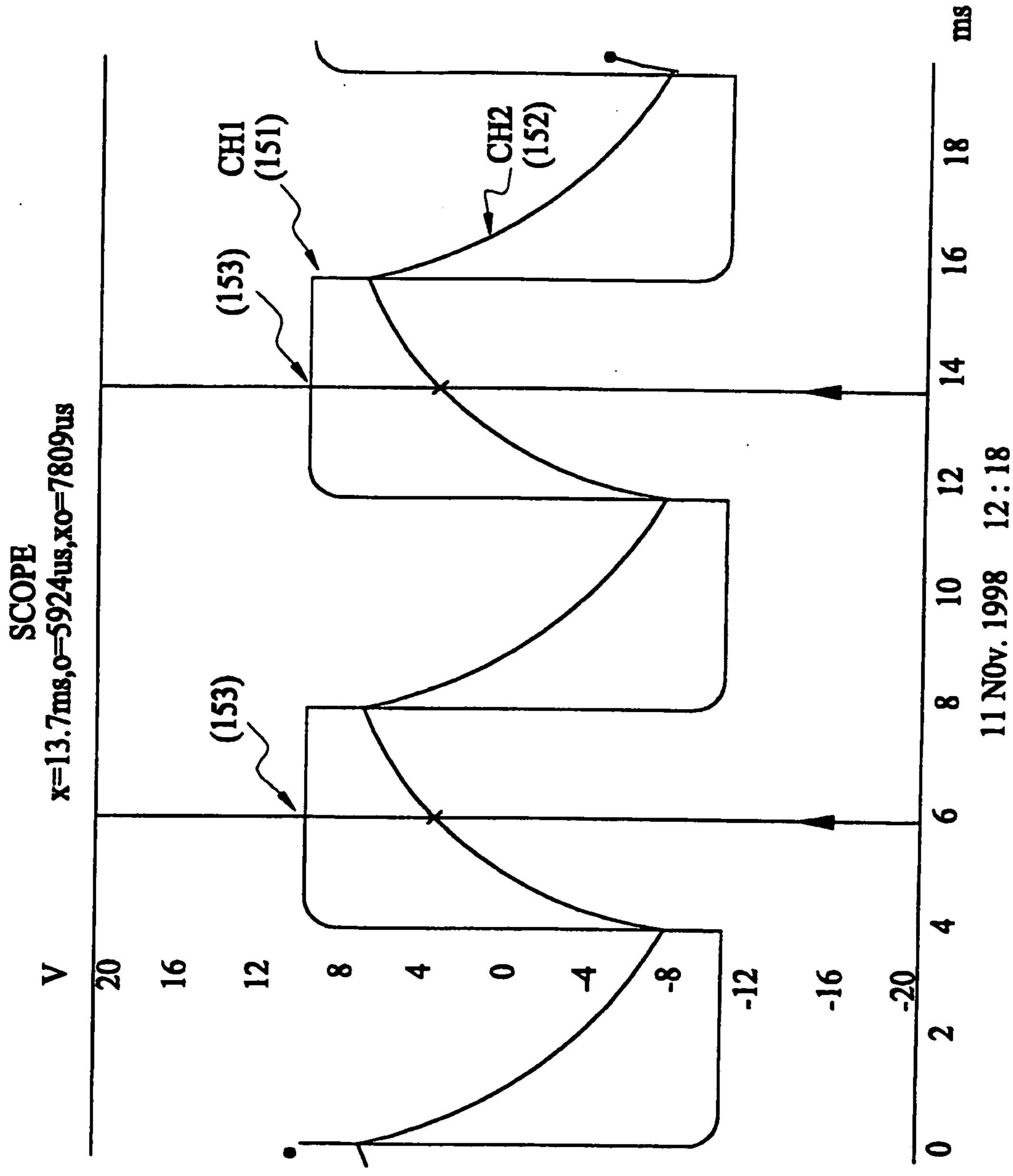


FIG. 14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V
20
16
12
8
4
0
-4
-8
-12
-16
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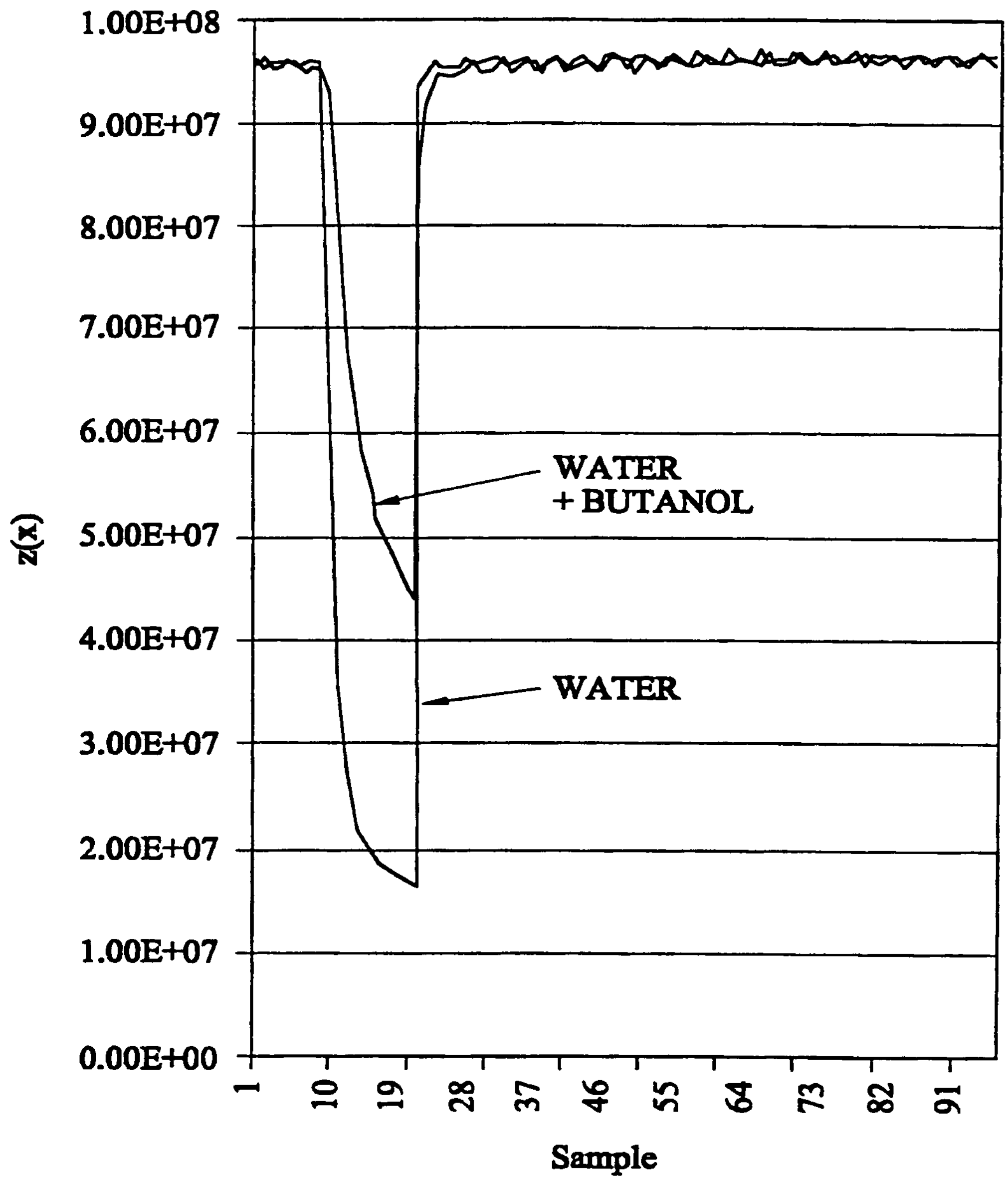
CH1
(151)
CH2
(152)
(153)
(153)
0
2
4
6
8
10
12
14
16
18
ms
11 N0v. 1998 12 : 18

FIG. 15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9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
z(x)
WATER
+ BUTANOL
WATER
1
10
19
28
37
46
55
64
73
82
91
Sample

FIG. 16

SENSOR 1

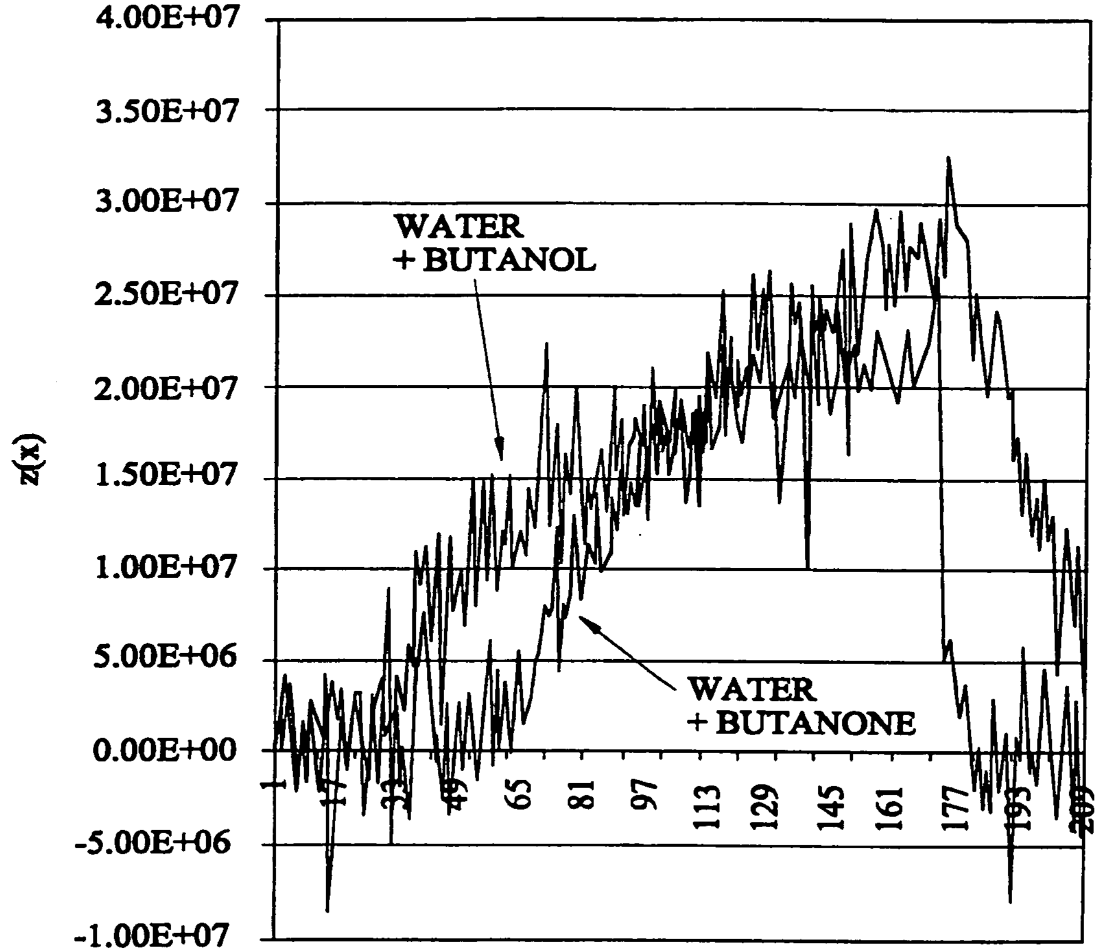


FIG. 17a

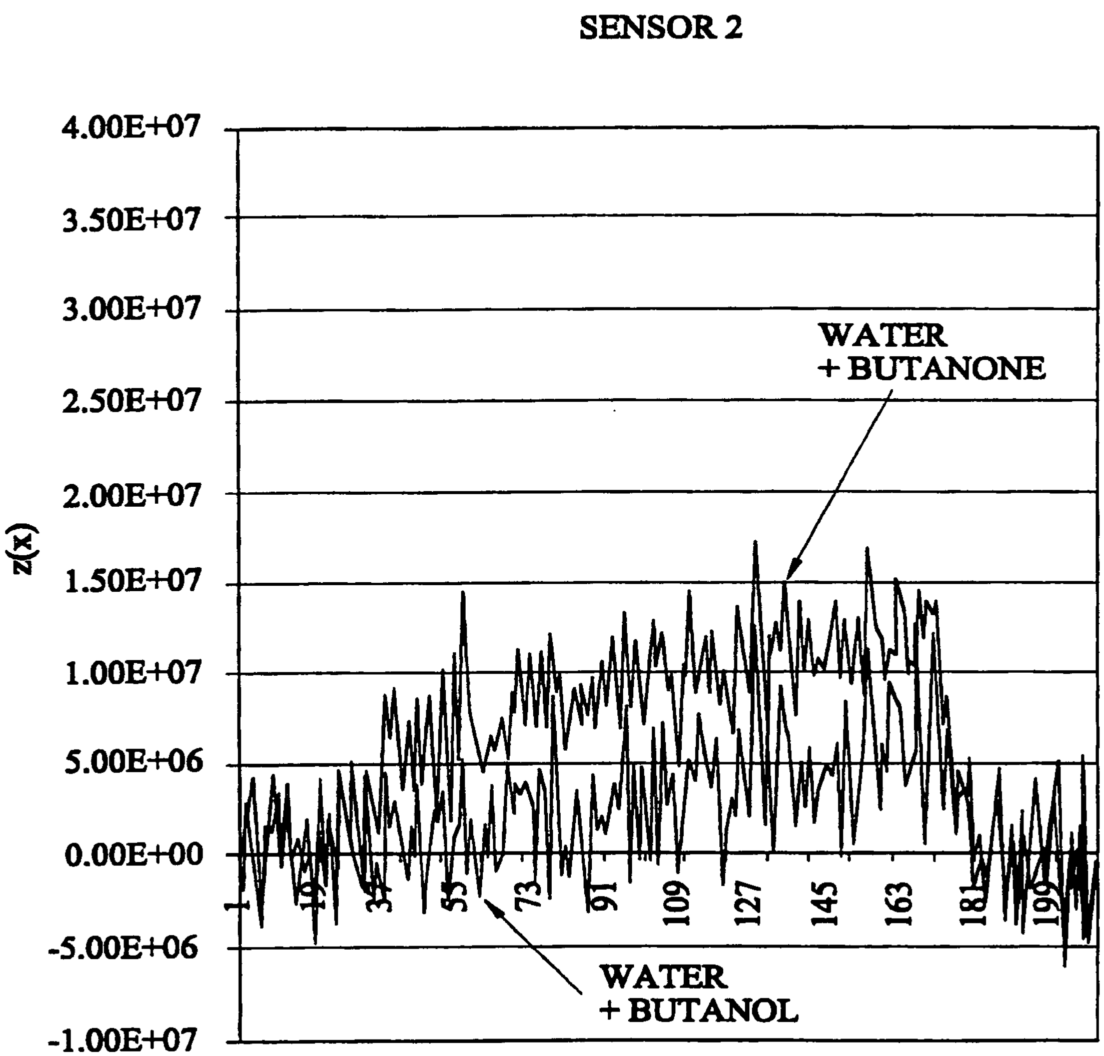
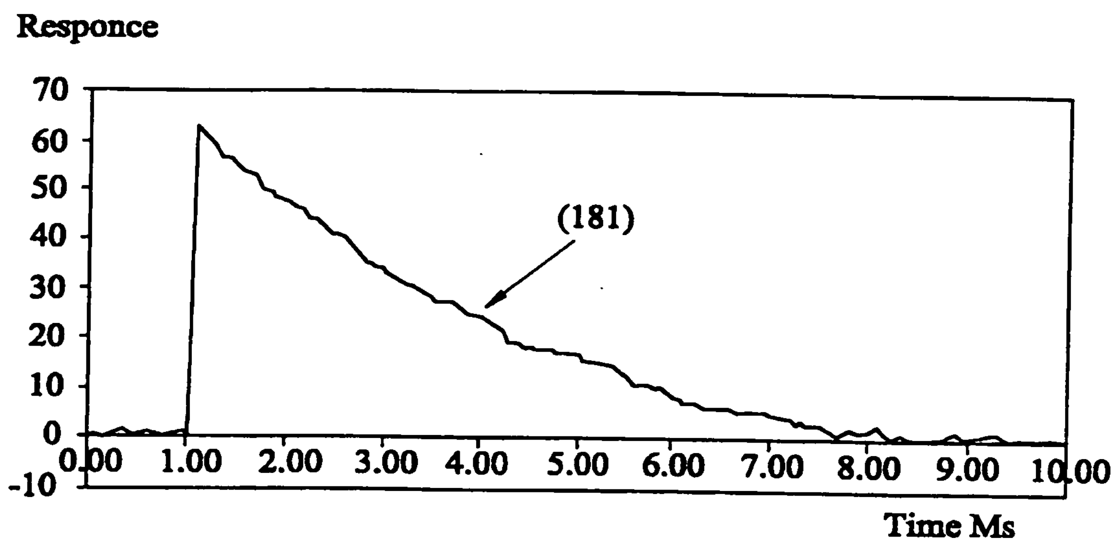

SENSOR 2
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
-5.00E+06
-1.00E+07
z(x)
1
19
37
55
73
91
109
127
145
163
181
199
WATER + BUTANONE
WATER + BUTANOL

FIG. 17b


Responce
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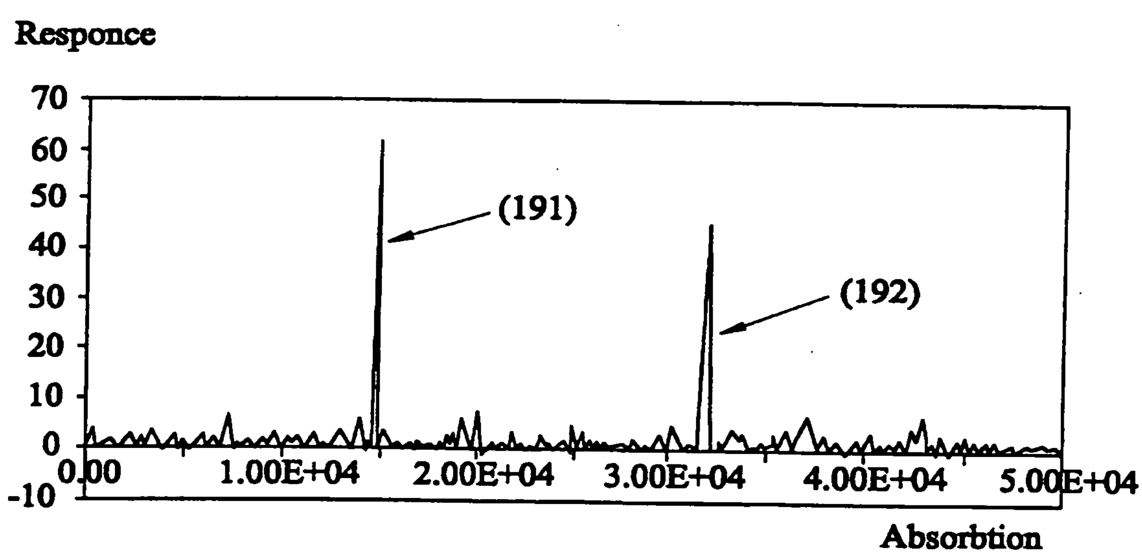
40
30
20
10
0
-10
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
(181)
Time Ms

FIG. 18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10
0
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0.00
1.00E+04
2.00E+04
3.00E+04
4.00E+04
5.00E+04
(191)
(192)
Absorbtion

FIG. 19